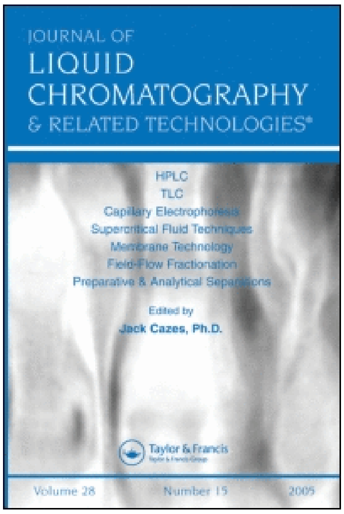

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APPLICATION OF HIGH PERFORMANCE LIQUID CHROMATOGRAPHY TO THE ANALYSIS OF NUCLEAR MATERIALS

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ABSTRACT

A small-particle (13 μm) styrene-divinylbenzene cation-exchange resin has been used for the separation and determination of trace metals in nuclear materials such as steels, Ni-Cr-Fe alloys, zirconium, and uranium. The eluted metal ions, which included Mn, Fe, Co, Ni, Cu, Zn and Pb, were monitored with a variable wavelength detector after a post-column reaction with 4-(2-pyridylazo)-resorcinol. The metal ions were determined at 10^{-4} to 1% (w/w) levels by direct injection of solutions of the materials. Interference from uranium, due to the reaction between uranium and the reagent used for detection, was removed either with a masking agent or by a coupled-column technique.

INTRODUCTION

The application of high-performance liquid chromatography (HPLC) to the separation and determination of metal ions has not received the same attention given to organic compounds and inorganic anions (Ion Chromatography). Some of the major reasons for this lack of interest have been: the availability of other instrumental methods of analysis such as atomic absorption and emission spectroscopy; the incompatibility between solvent systems normally used in analysis for metal ions and the materials used in high-performance systems; and the lack of suitable detectors for metal ions. Often the common instrumental methods used for the determinations of metal ions are susceptible to interferences and/or matrix effects and require a preliminary separation of the components of interest. In such situations, HPLC offers a fast method of sample pretreatment and could be used for the direct analysis of the sample if an appropriate detection system was available. Recently, there has been a significant increase in the number of publications in this area as the potential of HPLC for the separation and determination of metal ions and metal complexes is being recognized and answers are being found for some of the technical problems.

Some of the detection systems that have been used for the HPLC of metal ions include atomic absorption, UV-visible spectrophotometry, arc and inductively-coupled plasma emission spectrometry, oxidation-reduction at an electrode, and radioactivity monitoring. While all of these detection systems can provide useful information, the most promising systems for routine work are UV-visible and coulometric detectors. The post-column reaction system introduced by Fritz and his students (1-3), which is based on the formation of a metal complex having large molar absorptivity in the UV-visible region, is inherently flexible with regard to selectivity and sensitivity. Recent studies have shown that with slight modifications, this is an attractive detection system for HPLC (4-6) and this modified system has been used in this work. Coulometric detection has also been used extensively in HPLC and the work of Takata et al. (7-10) has shown that both direct and indirect coulometric detection can be used for metal ions.

This paper describes the results of a study of the potential of HPLC for the determination of trace amounts of metal ions in steel, nickel-chromium-iron alloys, zirconium alloy, and uranium. The emphasis in this report is on trace analysis since previous studies have shown that low to medium resolution systems can be used for the determination of major components in metals and alloys (11) and the transfer of these methods to HPLC should be, in many instances, a relatively simple matter.

METHODS

Dissolution of Nickel-Chromium-Iron Alloys and Steels. A 1-g sample of the alloy or steel chips was washed with acetone, weighed, and dissolved in 10 mL of concentrated double-distilled HCl at 90°C in a covered beaker. On dissolution, the solution was evaporated to near dryness under a stream of nitrogen, removed from the heat and diluted with 5 mL of distilled-deionized water and 1 mL of double-distilled HNO_3. This solution was transferred to a 50-mL volumetric flask and diluted to the mark with distilled-deionized water.

Dissolution of Zirconium. Zirconium turnings (∿ 1 g) were washed with methylene chloride and methanol, dried and weighed. For samples 1 and 2, 20 mL of 36 $mol.L^{-1}$ H_2SO_4 was added to the zirconium and the mixture was heated (∿ 100°C) with occasional addition of 1 mL of H_2O_2 (30%) to enhance dissolution. Upon complete conversion of the metal to the sulfate salt, the sample was fumed under a nitrogen purge to near dryness and the residue was dissolved up to 50 mL in distilled-deionized water.

For sample 3, 40 mL of 1 mol.L^{-1} HNO_3 and several drops of concentrated HF were added to the turnings and the sample was heated to ∿ 90°C. Additional HF was added periodically until dissolution was complete and the sample was diluted to 50 mL with distilled-deionized water.

MATERIALS

Apparatus. The HPLC system used has been described elsewhere (4,5). PAR (4-(2-pyridylazo)-resorcinol) was used for detection of the metal ions. This reagent solution which was $2x10^{-4}$ mol.L^{-1} PAR with 2 mol.L^{-1} ammonia and 1 mol.L^{-1} ammonium acetate, was mixed in a 1:1 (V/V) ratio with the column eluate in a low-dead-volume mixer (4) and the resulting solution was monitored at 540 nm.

Separations were done on 4 mm x 10 cm columns packed with 13 µm Aminex A-5 (Bio-Rad, Mississauga, Ont.) or a Brownlee bonded-phase ion exchanger (KAT 10 µm, Technical Marketing Associates, Mississauga, Ont., Canada). An aqueous suspension of the Aminex resin was homogenized ultrasonically and then slurry packed into stainless steel columns at 34 MPa (5000 psi).

For the coupled-column separation of uranium, a 2 x 3 mm Aminex cartridge (5) was placed in the sample loop position of a highpressure sampling valve and this valve was placed in the inlet side of the column. Samples were loaded onto this cartridge with a chemically inert pump (CMP-1, Laboratory Data Control, Riviera Beach, Fla.).

Samples. The UNS Ni-Cr-Fe alloys were supplied by Noranda Specialty Metals (Noranda Metal Industries Ltd., Arnprior, Ont., Canada). A detailed description of these alloys and the sampling techniques used has been given elsewhere (12).

The steel samples were British Chemical Standards (Bureau of Analyzed Samples, Middlesbrough, England) and the zirconium samples were from the EZ series of NBS standards which are described in NBS Publication 241, 1962, NBS, Washington, D.C. The high-purity zirconium bar, used for the preparation of standard curves, was purchased from the Materials Research Corporation (Orangeburg, N.Y.).

RESULTS AND DISCUSSION

Ferrous and Nickel-Chromium-Iron Alloys. In nuclear-power reactors the in-core activation of cobalt to ^{60}Co, which emits a very penetrating γ-radiation, and the subsequent transport of Co in heat transport fluids to and deposition onto out-of-core components, is an important factor in the production of radiation fields in these out-of-core components. Consequently, accurate and sensitive analysis procedures for cobalt in materials that are in contact with heat-transport fluids are important to both the manufacturer of reactor components and the designer. Some example HPLC separations

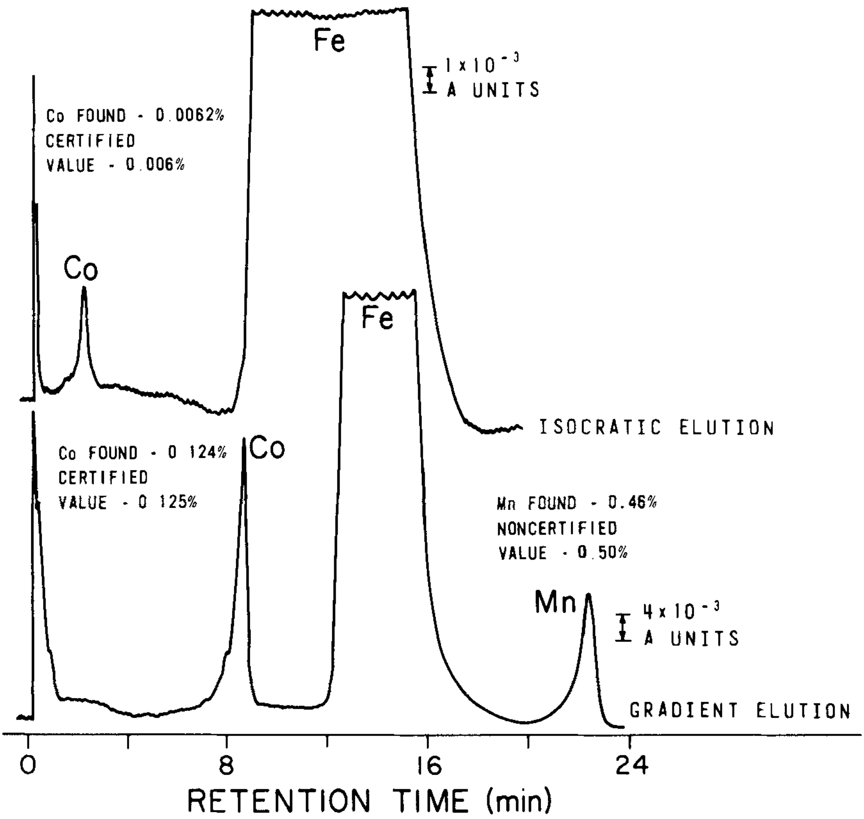

FIGURE 1
HPLC analysis of steels. Experimental conditions: sample, 10 μL of ∿12 $mg.mL^{-1}$ steel solution; Aminex column; detection at 540 nm, post-column reagent, 50 $\mu g.mL^{-1}$ PAR solution in 2 $mol.L^{-1}$ ammonia and 1 $mol.L^{-1}$ ammonium acetate at flow-rate of 1.5 mL min^{-1}; eluent flow, 1.5 $mL.min^{-1}$; isocratic conditions, 0.07 $mol.L^{-1}$ citrate at pH 4.8; gradient conditions, 0.001 to 0.10 $mol.L^{-1}$ citrate at pH 4.8.

of ferrous alloys are shown in Figure 1. These chromatograms show that both isocratic and gradient conditions can be used and that large iron concentrations (12 $mg.mL^{-1}$) can be injected, thus permitting the determination of small concentrations of Co(II).

TABLE 1

ANALYSIS OF STEELS AND Ni-Cr-Fe ALLOYS*

Sample	Co Found by HPLC (wt%)	Certified Analysis (wt%)	Analysis _Not_ Certified (wt%)	Mn Found by HPLC (wt%)	Analysis _Not_ Certified (wt%)
Steel Sample					
BAS327 SS57	0.0062	0.006		0.407	
BAS272 SS12	0.251	0.250		0.488	0.54
BAS273 SS13	0.027	0.021		0.440	0.49
BAS274 SS14	0.194	0.190		0.444	0.52
BAS276 SS16	0.027	0.027		0.477	0.48
BAS277 SS17	0.124	0.125		0.455	0.50
Ni-Cr-Fe Alloy					
Incoloy B	0.018		0.020**	0.690	
UNS N08800A	0.011	0.011			
UNS N08800B	0.019	0.019			
UNS N06600	0.0073	0.0078			

* The analysis conditions for the steels are given in Figure I and for the Ni-Cr-Fe alloys in Figure 3; all calculations done on the basis of peak heights.

** Determined by atomic absorption spectrometry.

Gradient elution is preferred for the determination of more than one metal while isocratic elution is preferred for maximum baseline stability. Table I summarizes the results obtained for Co(II) and Mn(II) in a number of steel standards. In each case there was excellent agreement between the certified value for Co(II) and the result found by HPLC. The agreement between the HPLC results for Mn(II) and the values supplied with the standards is not as good but the reliability of the values given for the standard is uncertain since these standards were not certified for Mn(II).

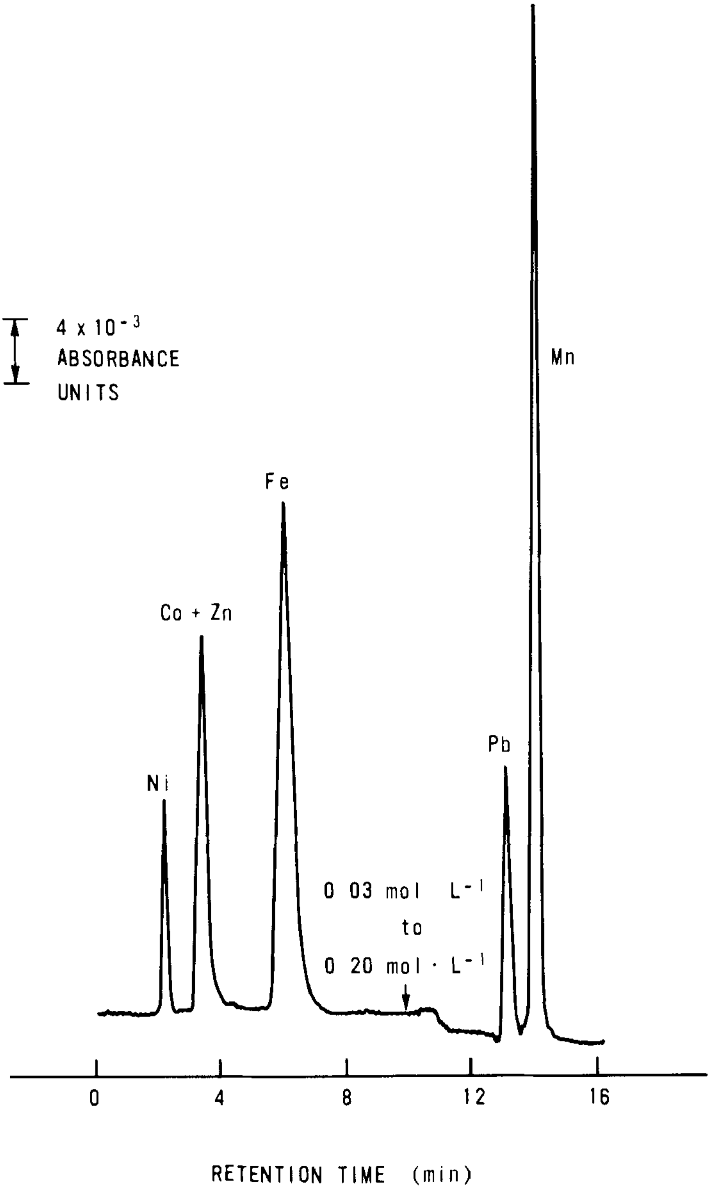

FIGURE 2

HPLC separation of metal ions on bonded-phase ion-exchanger. Experimental conditions: sample, 10 µL of a solution containing 5 to 100 µg.mL^{-1} of each metal ion; 10 µm Brownlee column; eluent, step gradient of citrate (pH 4.6) from 0.03 to 0.2 mol.L^{-1}; eluent flow, 1.0 mL.min^{-1}; detection as for Figure 1.

During this investigation of the HPLC determination of cobalt in Ni-Cr-Fe alloys, a bonded-phase ion-exchanger was also studied briefly. Figure 2 shows that although good peak shapes were obtained with this column, Co(II) and Zn(II) could not be separated. The low capacity of this bonded phase was another factor limiting its use for these samples since small concentrations of eluents must be used and this reduces the buffering capacity of the eluent, an important factor when large concentrations of acidic samples are injected. For some metal ions, particularly Fe(II) and Mn(II), the limit of detection improved when the bonded phase column was used, presumably due to a more favourable reaction with the post-column reagent, PAR, in the presence of the lower concentrations of citrate used to elute the metal ions. Satisfactory separations were obtained with pH-gradients for both the bonded phase and Aminex columns but this mode was not used since it tended to decrease baseline stability.

With the Aminex columns, the citrate eluent did not give a satisfactory separation of very small amounts of Co(II) (or Cu(II)) in the presence of large concentrations of Ni(II); a tartrate eluent gave improved separations, as shown in Figure 3. The tartrate eluent was maintained at pH 3.5 since the separation of some of the metal ions deteriorated at pH values above 3.5, and at lower pH values the solubility of the tartrate decreased (acid salts of tartaric acid are only slightly soluble).

Large concentrations (0.2 mg in 10 μL injection) of Ni(II) had no effect on the linear calibration curve of Co(II); the working

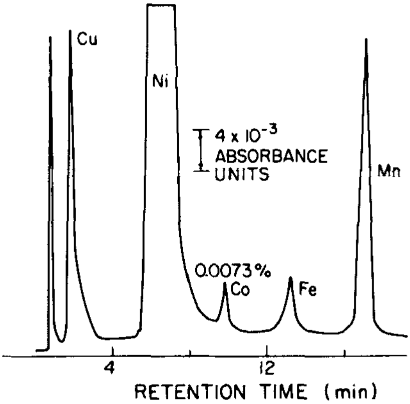

FIGURE 3
HPLC analysis of nickel-chromium-iron alloy. Experimental conditions: sample, 10 μL of 20 mg.mL^{-1} solution; Aminex column; eluent, linear gradient from 0.2 to 0.4 mol.L^{-1} tartrate (pH 3.5) over 15 min; eluent flow, 1 mL.min^{-1}; detection as for Figure 1.

range studied for Co(II) was 10 to 50 ng and the detection limit (2X baseline noise) under these conditions was ∿1 ng.

A summary of the results for the determination of Co(II) in a number of Ni-Cr-Fe alloys is shown in Table 1. The UNS alloys were the subject of an interlaboratory comparison between eleven laboratories. The results of this study have been given elsewhere (12) and the certified results given for the UNS alloys in Table 1 are those given in this interlabortaory comparison (12). The 'uncertified' results for Incoloy B are atomic absorption results from our laboratories. The results in Table I show that there is excellent agreement between the HPLC results and the accepted values for Co(II) in these Ni-Cr-Fe alloys.

Uranium. Figure 4 shows that when a concentrated uranium solution was injected directly onto the column, the reaction between the

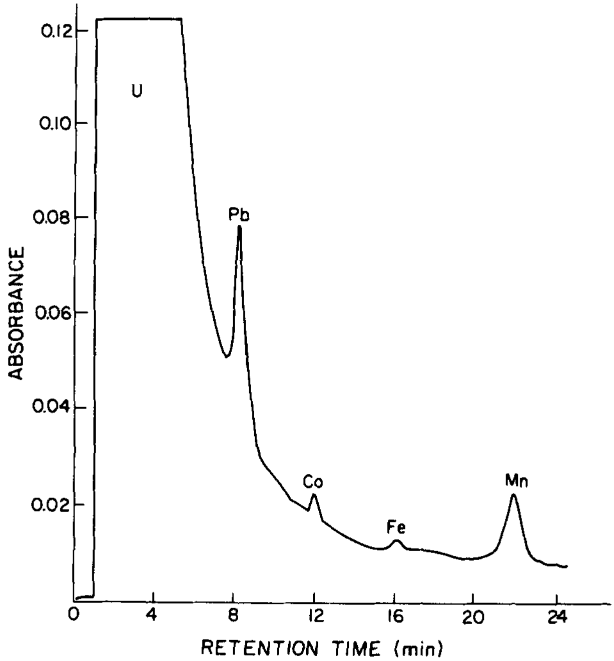

FIGURE 4
HPLC analysis of uranium. Experimental conditions: sample, 10 μL of 357 mg.mL^{-1} uranium solution, Aminex column; eluent, linear gradient from 0.3 to 0.5 mol.L^{-1} tartrate (pH 3.5) over 15 min; eluent flow, 1 mL.min^{-1}, detection as for Figure 1.

eluted uranium and PAR interfered with the determination of trace amounts of other metal ions. One technique that can be used to remove interferences with post-column-reaction detection is the addition of a masking agent to the post-column reagent. Carbonate forms a stable complex with uranium and studies showed that the uranium-PAR reaction was almost completely inhibited in the presence of 0.3 mol.L^{-1} carbonate. Figure 5 shows that the carbonate had little or no influence on the reaction between PAR and the other metal ions studied. A comparison of Figure 4 with Figure 6, which

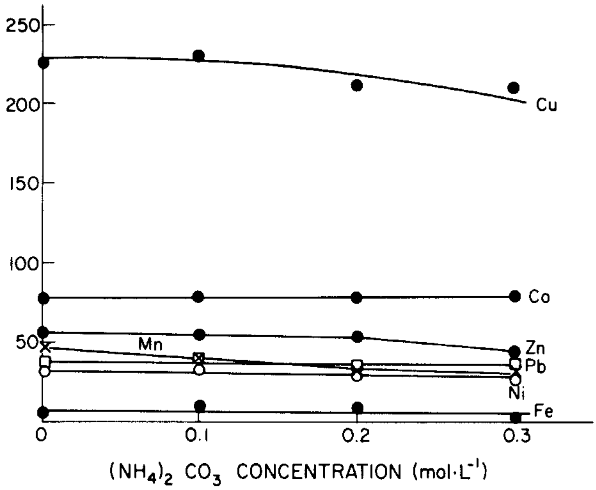

FIGURE 5
Effect of carbonate on the reaction between PAR and eluted metal ions. Experimental conditions similar to those given for Figure 4; detection as for Figure 1 plus the addition of carbonate to the post-column-reagent solution.

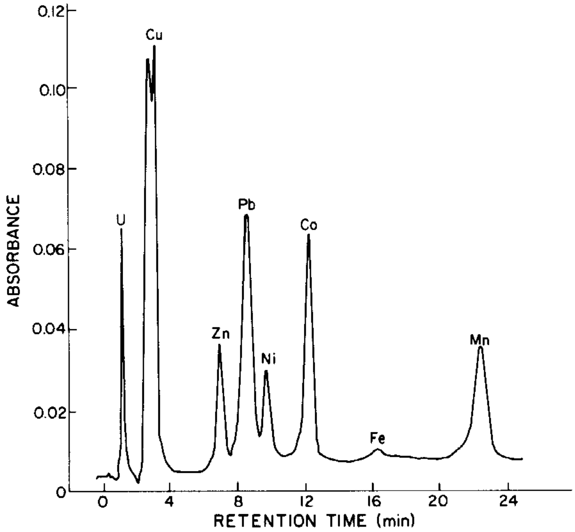

FIGURE 6
HPLC analysis of uranium with 0.3 mol.L^{-1} carbonate in post-column-reagent solution. Experimental conditions as for Figure 5.

shows the chromatogram obtained with 0.3 mol.L^{-1} carbonate added to the post-column reagent, clearly illustrates the improved detection of the metal ion impurities in the presence of carbonate.

The effect of the carbonate masking agent on the analysis of uranium is shown in Table 2. The improved determination of Zn(II) is evident. Since the peak shape or Cu(II) is affected by the large concentrations of uranium co-eluting with Cu(II), the results for Cu(II), calculated on the basis of peak height, are low; peak area

TABLE 2

HPLC ANALYSIS OF URANIUM*

Metal	ng added	SAMPLE A** ng found			
		0.0 mol.L^{-1} $CO_3^=$	0.1 mol.L^{-1} $CO_3^=$	0.2 mol.L^{-1} $CO_3^=$	0.3 mol.L^{-1} $CO_3^=$
Cu	0	ND$^+$	28	44	45
Zn	0	ND	10	15	10
Pb	0	290	300	310	300
Ni	0	ND	14	18	10
Co	0	4.2	45	45	46
Mn	0	43	41	45	43
		SAMPLE B* ng recovered			
Cu	200	ND	130	140	160
Zn	200	ND	203	205	198
Pb	200	213	207	215	194
Ni	500	540	520	530	540
Co	50	53	54	54	52
Mn	100	102	108	105	100

*Experimental conditions as for Figure 6; all calculations done on the basis of peak heights.

**Samples A and B were reagent purity uranium. Sample B was spiked with the metal ions shown. Both injections contained 3.6 mg of uranium.

$^+$ND = Not Detected.

measurements should improve Cu(II) analytical results and possibly those for the rest of the metal ions studied. However, the results shown in Figure 6 and Table 2 illustrate the effectiveness of the combination of masking agents and post-column reactions for the detection of metal ions.

The second approach used to remove this interference from uranium was a coupled-column technique. A 1-mL sample of the uranium in 9:1 (V/V) tetrahydrofuran-concentrated nitric acid was pumped through a 2 x 3 mm bed of Aminex resin and this bed was then valved into an aqueous tartrate eluant flowing onto the main separator column. In tetrahydrofuran-nitric acid, U(VI) forms a stable tetrahydrofuran-nitrate complex (13), which is not retained on a strong sulfonic-acid exchanger, whereas most other metal ions are strongly retained; these metal impurities can then be eluted onto another cation-exchange column and separated (Figure 7). A comparison of Figure 4 and Figure 7 illustrates the improved chromatography obtained with this coupled-column approach. Studies of this system indicated >99% removal of the U(VI) and 100% recovery for Pb(II), Co(II), Fe(III) and Mn(II). Lower recoveries were obtained for Cu(II), Ni(II) and Zn(II) but the use of a larger sampling cartridge and/or a change in the composition of the sampling medium should improve the recoveries for these metal ions.

Zirconium. Extensive use is made of zirconium and zirconium alloys in nuclear-power reactors and the analysis for trace elements in these metals is difficult and often requires a preliminary separation. Due to the complex aqueous chemistry of zirconium and

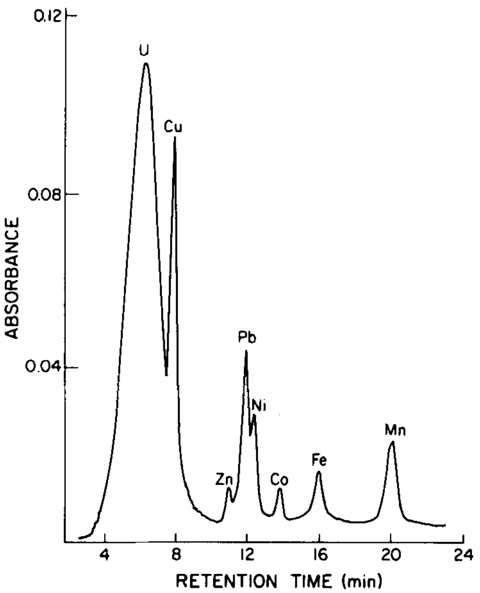

FIGURE 7
HPLC analysis of uranium with a coupled column technique. Experimental conditions: sample, 1 mL of 5 mg.mL^{-1} uranium solution in 9:1 tetrahydrofuran concentrated nitric acid; coupled 2 x 3 mm and 4 x 130 mm Aminex columns; eluent, linear gradient from 0.05 to 0.45 mol.L^{-1} tartrate (ph 3.6) over 15 min; eluent flow, 1 mL.min^{-1}; detection as for Figure 1.

its strong tendency to form polymeric hydrolysis products, it was felt that the analysis of these samples would provide a "worst case" situation for the HPLC analysis for trace elements in metals and alloys.

An example separation of a zirconium standard is shown in Figure 8. Calibration curves obtained in the presence of large concentrations of zirconium were linear for all of the metal ions studied (Figure 9). The shape and retention time for the Cu(II) peak was variable, likely due to the co-elution of the large concentration

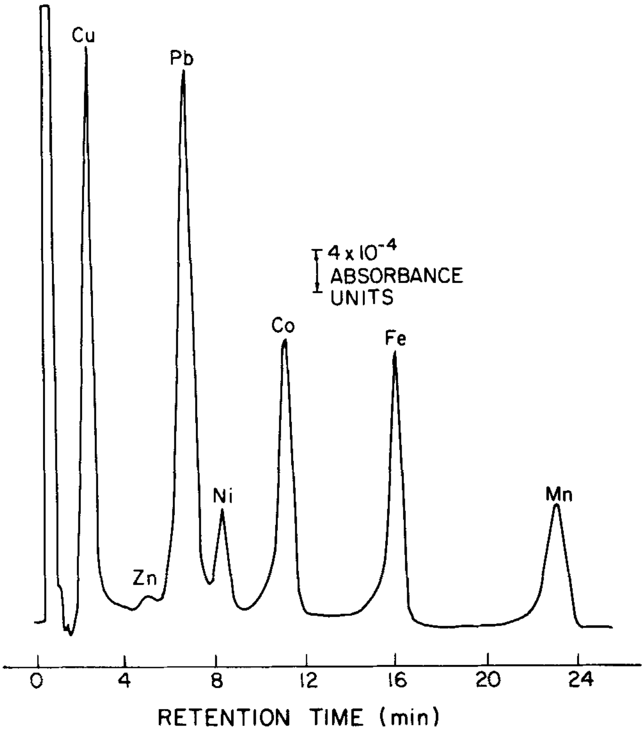

FIGURE 8
HPLC analysis of zirconium. Experimental conditions: sample, 20 µL of 85 $mg.mL^{-1}$ EZ-10 standard; Aminex column; eluent, linear gradient from 0.35 to 0.5 $mol.L^{-1}$ tartrate (pH 3.5) over 15 min; eluent flow, 1 $mL.min^{-1}$; detection as for Figure 1.

of zirconium (zirconium does not react with PAR). Consequently, the results for Cu(II) (Table 3) in a standard zirconium alloy were variable but still acceptable since the results were calculated on the basis of peak height. The results for Co(II) and Mn(II) are quite good, but erratic results were obtained for Pb(II) and Ni(II) when a tartrate eluent was used. The use of a citrate buffer gave acceptable values for Pb(II) and these results agreed with atomic

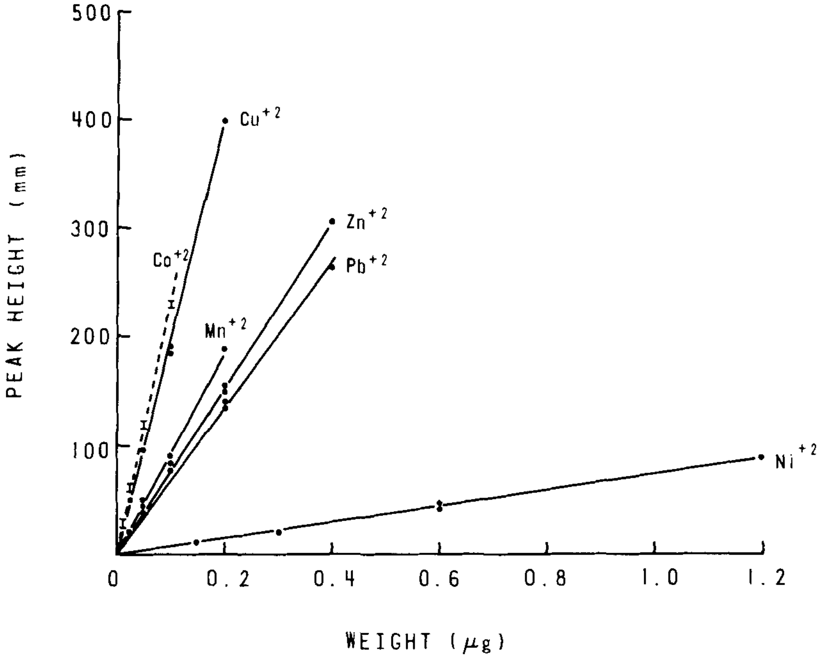

FIGURE 9
Calibration curves in the presence of 37 $mg.mL^{-1}$ zirconium. Experimental conditions as for Figure 8.

TABLE 3

HPLC ANALYSIS OF ZIRCONIUM*

		HPLC Result ($\mu g.g^{-1}$)				
Metal	Emission Spectrographic Analysis ($\mu g.g^{-1}$)	Tartrate Buffer			Citrate Buffer	
		Sample 1	Sample 2	Sample 3	Sample 2	Sample 3
Cu	112	130	110			
Zn	-	3	7	6		
Pb	175	380	350	410	200	170
Ni	950	290	550	490		
Co	52	48	48	57		
Mn	52	53	52	58	56	52

*Experimental conditions as for Figure 8. Zirconium concentrations in samples 1, 2 and 3 were 85, 46 and 20 $mg.mL^{-1}$ respectively.

absorption results. The citrate system could not be used for Ni(II) since Ni(II) elutes near the solvent-front peak. The reason for the poor results for Pb(II) and Ni(II) in the citrate eluent is unclear but may be associated with the formation of kinetically stable complexes during the dissolution procedure; it is interesting to note that the Pb(II) results are consistently low and the Ni(II) results consistently high. The EZ zirconium standards contain small amounts (∿1% w/w) of tin, and hydrolysis of the tin might cause the problems encountered with Pb(II) and Ni(II). Other complexing agents could possibly provide better chromatographic results for all metal ions but this was not investigated.

CONCLUSIONS

These results show that high performance liquid chromatography can be used for the rapid and accurate analysis of metals and alloys for trace impurities at the 10^{-4} to 1% levels. With the proper choice of complexing agents as eluents, problems related to hydrolysis of metal ions can be eliminated or minimized. The use of complexing eluents in place of strong acids also permits operation at intermediate pH values (pH2-pH7), which will minimize corrosion of pump components and prolong the life of bonded-phase columns. The selectivity of post-column detection can be improved through the use of masking agents and/or the use of coupled column techniques. Since the large concentrations of matrix components can affect peak shapes for some metal ions, peak area measurements are preferred for quantitation.

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